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(54) Title: USE OF ETHER CARBOXYLATES AS LUBRICANTS

(57) Abstract: Use of ether carboxylates with an average ethoxylation degree of between 0.3 and 15 as lubricants. More specifically, the invention refers to the use of these ether carboxylates as lubricants in conveyor systems for glass and/or plastic bottles, such as polyethylene-terepthalate (PET) or polycarbonate (PC); cans, glass containers, drums, cardboard containers and similar items.

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USE OF ETHER CARBOXYLATES AS LUBRICANTS

Field of the invention

The present invention refers to the use of ether carboxylates with an average ethoxylation degree of between 0.3 and 15 as lubricant agents. More specifically, the invention refers to the use of these ether carboxylates as lubricants in conveyor systems for glass and/or plastic bottles, such as polyethylene terepthalate (PET) or polycarbonate (PC); cans, glass containers, drums, cardboard containers and similar items.

State of the art of the technique

Usually, in bottle and barrel plants of drinks' manufacturers and in food packaging, articulated plate conveyor belts or other transport systems are used that are maintained lubricated and cleaned with the aid of appropriate aqueous lubricant agents, preferentially applied with automatic lubrication systems for conveyor belts, equipped with a sprayer system.

Normally, for this purpose soap-based lubricants are used (based on inorganic or organic alkaline salts of a fatty acid or a mixture of fatty acids that contain a minimum of 8 carbon atoms). However, these lubricants present several disadvantages:

- To complex the water hardness the lubricants must contain the corresponding amounts of ethylendiamino-tetraacetic or nitrylotriacetic acid. This prevents the formation of calcium salts that can block the nozzle of the lubrication system.

- For harder waters, larger amounts of complexing agent are required in the lubricant preparations, making it necessary to reduce the soap contents in the finished product. However, this reduces the lubricant effect of the preparation.

- Soap-based lubricant preparations have a relatively intense foam production since it is very difficult to defoam soaps that have already formed. The excess foam produced by the lubricant is lost when lubricating the conveyor belts and can penetrate the goods transported. On the other hand, foam production on conveyor belts hinders the automatic control of these recipients.

- The use of softened water to prevent calcium soap foam formation in products with no complexing agent or with only a reduced amount, increases the cost of using these products.

- The compound ethylendiaminotetraacetic acid (EDTA) is not very biodegradable.

Because of these drawbacks, soap-based lubricants have been increasingly replaced by lubricants based on fatty amines and derivatives or lubricant compounds based on phosphoric esters.

For example, application for the European patent EP-A-0044458 describes mainly soapfree lubricants adapted for use as conveyor belt lubricants that consist of:

a) a non ionic carboxylate compound of general formula $R-[O-(CH_2)_m]_n-COOM$
wherein
R is a saturated or unsaturated alkyl group, m = 2-3, n = 3-7 and M is H, an alkaline metal or an alkanol amine cation,

b) an acylsarcosinate of general formula $RCON(CH_3)CH_2COOM$
wherein
R is an alkyl or alkenyl group C_{11}-C_{19}, and M is H, an alkaline metal or alkanol amine cation, and

c) water, and optionally a conventional non-ionic surfactant that presents a HLB value between 10 and 12 to improve the detergency.

In said patent application, it is specified that the mean ethoxylation

degree of the non ionic carboxylate compound must not be lower than 3 or above 7. On the other hand, in the examples non-ionic carboxylate compounds are described with an average ethoxylation degree of 5.

The patent application DE-A-4244536 describes lubricant compositions for bottle conveyor belts that contain an N-alkyldiamine, its salt obtained with an organic acid and, optionally, an organic acid and an ether carboxylate of formula $R-(OC_2H_4)_xO(CH_2)_yCOOH$, wherein R is an alkyl group 10-20C (preferably 16-18C), x = 1-20 (preferably 5-15) and finally y = 0-5 (preferably 1). However, in all the examples ether carboxylates with an average ethoxylation degree of 9 are described.

In the international patent application WO-A-9519412 a lubricant composition is described with biocide properties comprised by (a) a cyclic imidazoline as the active lubricant ingredient, (b) an acid to maintain this imidazoline water-soluble and, optionally, (c) a non ionic surfactant, an alkylaminocarboxylate and non-ionic surfactants such as ether carboxylates of general formula $R-(OC_2H_4)_nOCH_2COOH$, in which R is $CH_3-(CH_2)_m-$, wherein m is zero or a whole number between 1 and 20, preferably between 2 and 17; an unsaturated carbon chain C_2-C_{20}; or a branched saturated or unsaturated chain; n is a whole number between 1 and 30, preferably between 2 and 9. In the international patent application mentioned, R is preferably an oleic group and n is 9. On the other hand, in this international patent application it is mentioned that the function of component (c) is, primarily, to reduce the foam and to improve the properties of the final lubricant composition in dealing with dirt by emulsifying this dirt and, secondly, by facilitating the solubilization or the dissolution of component (a).

Finally, patent application DE-A-19642598 describes a lubricant concentrate for conveyor belt installations in the food industry, based on amines comprised by: i) one or more amines, ii) one or more ether carboxylates, iii) one or more polyethylene glycols and iv) up to 99% in weight of the usual additives and adjuvants. The ether carboxylates described in this patent application are compounds of general formula

$R-(O(CH_2)_m)_nOCH_2COO^-M^+$

wherein

R is a saturated alkyl residue, linear or branched containing from 1 to 22 carbon atoms or an alkylaryl residue or mono alkynyl or polyunsaturated

linear or branched residue contained from 2 to 22 carbon atoms, or a mono aryl residue or an alkyl poly C_1-C_{22}, mono or poly C_2-C_{22} alkenyl or alkynyl residue

m is 2 or 3,

n is a positive whole number between 1 and 30,

M is hydrogen or an alkaline metal.

In the mentioned patent application it is specified that R is preferably an oleic group and n is 9.

However, to the knowledge of the authors of this invention, ether carboxylates with an average ethoxylation degree of between 0.3 and 15 have not been used as a lubricant; or specifically in conveyer systems for glass and/or plastic bottles, such as, bottles of polyethylene terephtalate (PET) or polycarbonate (PC); cans, glass containers, drums, cardboard packaging and similar items. On the other hand, these ether carboxylates can provide a simple and versatile way to lubricate conveyor systems achieving, at the same time, an unexpected bactericide activity without having to add additional ingredients.

Description of the invention

The object of the invention is the use of ether carboxylates with an average ethoxylation degree of between 0.3 and 15 as a lubricating agent. Specifically, the ether carboxylates of the invention are used to lubricate conveyor systems for glass and/or plastic bottles, such as, for example, polyethylene terephtalate (PET) or polycarbonate bottles (PC); cans, glass containers, drums, cardboard packaging or similar items.

In one specific application, ether carboxylates are defined according to general formula (I):

$$R\text{-}(OCH_2CH_2)_n\text{-}O\text{-}CH_2COOX \qquad (I)$$

wherein

- R is an alkyl, alkenyl or alkynyl residue containing from 12 to 22 carbon atoms,

- n is a number between 0.3 and 15,
- X is hydrogen, an alkaline metal, alkaline metal, an ammonium cation or an hydroxyalkylammonium cation.

Preferably, in the ether carboxylates of general formula (I), R represents an alkyl, alkenyl or alkynyl residue that contains 16 to 18 carbon atoms.

Also, ether carboxylates of general formula (I) are preferred in which n is a number between 0.3 and 10, preferably between 0.5 and 6, more preferably between 0.5 and 3.

Finally, ether carboxylates of general formula (I) in which X is hydrogen or an alkaline metal are also preferred.

Ether carboxylates of general formula (I) can be obtained, for example, as described in the European patent application EP-A-0580263. The process to obtain it consists of two steps, the first corresponding to the reaction of an alcohol containing a hydrocarbon chain of the desired length with ethylene oxide in the normal reaction conditions known by experts in this area. On the other hand, one can also start with a previously ethoxylated alcohol. Next, the ethoxylated alcohol is made to react with a strong base such as sodium or potassium hydroxide in the presence of a reducing agent, such as sodium borohydride, to form the corresponding sodium or potassium alkoxylate. This product is made to react with sodium monochloroacetate to form the corresponding ether carboxylate in salt form. This salt is transformed into the corresponding acid by washing with sulphuric acid or hydrochloric acid. The ether carboxylate obtained thus, which can also contain non ethoxylated alcohol, ethoxylated alcohol, carboxymethylated alcohol and esters of carboxymethylated acids with any of the substances with an alcohol function, can be purified using standard methods. Nevertheless, this purification is not essential for the use of ether carboxylate as a lubricant.

The ether carboxylates of the present invention are used in the aqueous form as a lubricant. Specifically, when they are used as lubricants for

conveyor systems for glass and/or plastic bottles, such as, for example, polyethylene terephtalate (PET) or polycarbonate bottles (PC); cans, glass containers, drums, cardboard packaging or similar items, the aqueous solutions contain between 0.1 and 30% in weight of ether carboxylate, preferably between 1 and 20% in weight. In this case the aqueous solution is considered to be in concentrated form.

Aqueous solutions of ether carboxylates, specifically when used for transport systems, can also contain additives such as ionic surfactants, non ionic surfactants, amphoteric surfactants, foam inhibitor agents, foam regulators, foam stabilizers, complexing agents, chelating agents, solubilizers, emulsifiers, biocides, bactericides, disinfectants, fungicides, antioxidants, corrosion inhibitors and pH regulators, thus forming concentrated aqueous lubricant preparations.

The pH of these lubricant preparations, especially when these are used for conveyor systems, is preferably between 3.0 and 9.0, even more preferably between 6.5 and 8.0.

Aqueous lubricant preparations are usually applied in very dilute form such that the active concentration applied in the conveyor systems ranges from 0.01% and 2% in weight. Therefore, the total contents of ether carboxylate present in the diluted aqueous preparations ranges from 0.01 to 1%, preferably between 0.02 and 0.5%. Dilution of the concentrated aqueous lubricant preparations to obtain diluted aqueous lubricant preparations, which are those that are directly applied to the conveyor systems can be done with hard water, semi-hard water or soft water.

The exact dilution of concentrated aqueous lubricant preparation will depend on several factors, such as, the displacement rate of the conveyor guide, the type of containers the guide transports etc.

As solubilizing agents, the compositions of the invention present solubilizing agents that can be mixed with water or that are water-soluble. Preferably, especially when the compositions are used for conveyor systems,

the following solubilizers are used urea, ethanol, n-propanol, i-propanol, n-butanol, ethyleneglycol and/or butyldiglycol, polyethylene glycols, vegetable oils, alkoxylated glycerine esters derived from carboxylic acids containing between 6 and 22 carbons such as those commercialized for KAO Corporation S.A. under the trademark Levenol, ether carboxylates with a carbonated chain C_2-C_{10}, etc., in an amount corresponding to between 10 and 40% in weight of one or several of these solubilizing agents, relative to 100 parts in weight of the total amount of general formula I ether carboxylates. These solubilizing agents are appropriate, in the context of the present invention, provided that they do not reduce the lubricant effect of the aqueous lubricant preparations.

The disinfectants that could be contained in the aqueous lubricant preparations, especially for conveyor systems, are, for example, those described in the "Guia de Plaguicidas utilizados en higiene alimentaria y salud publica" published by the Spanish Health Ministry (ISBN: 84-7607-499-2). Preferably, according to the invention bactericide products should be used when there is a risk of germs in the reserve tanks or on the conveyor belts. These disinfectants or mixtures of these can be used in amounts of 5 to 50 parts in weight, relative to 100 parts in weight of general formula I ether carboxylates.

The following examples are given to provide experts in the area a clear and complete description of the present invention.

Examples

Example 1. Lubrication in conveyor belt systems for bottles.

Tests to measure friction resistance were performed on a stainless steel bottle conveyor belt under the following conditions:

- Measurement of the resistance of 7 beer bottles type NRW 0.5 L, filled with water, as a tensile force using a dynamometer. These bottles are arranged in a plastic crate for beer that permits their rotation on the belt but prevents them from toppling over.
- Speed of bottles: approximately 0.5 m/s.

- Continuous spraying of the bottle conveyor belt with a lubricant solution of 0.04% in weight.
- Spraying volume of the nozzle: approximately 3.5 L/hour.

The friction coefficient (μ) is defined as the coefficient between the tensile force measured for a bottle and the weight of a bottle expressed in grams. This coefficient is determined when a constant value is obtained.

Foam production is controlled visually.

Dilution of ether carboxylates to obtain the aqueous lubricant compositions described in Table 1 is carried out with hard water, specifically of hardness 15°dH (German degrees) according to the regulation UNE-EN 12829.

Table 1. – Lubricant compositions for conveyor belts (LCC)

LCC	Lubricant	% in weight
LCC.1	Oleic ether carboxylate with an average ethoxylation degree of 1	0.04
LCC.2	Oleic ether carboxylate with an average ethoxylation degree of 2	0.04
LCC.3	Oleic ether carboxylate with an average ethoxylation degree of 1 in the form of a potassium salt	0.04
LCC.4	Oleic ether carboxylate with an average ethoxylation degree of 1.5 in form of potassium salt	0.04
LCC.5	Oleic ether carboxylate with an average ethoxylation degree of 2 in the form of potassium salt	0.04
Comparative example 1	N-9-octadecenylpropane-1,3-diamine	0.04
Comparative example 2	[1]Soap-based lubricant composition (tall oil acid neutralised with triethanolamine)	[2]0.25

[1]The composition of the soap-based lubricant presents the following

ingredients:

4.0 % in weight of tall oil acid.

9.5 % in weight of AKYPO® RO 50 VG[3]

6.5 % in weight of a mixture of ether carboxylate of octanoic acid with an average ethoxylation degree of 8 and an ether carboxylate of hexanoic acid with an average ethoxylation degree of 3.

2.0 % in weight of sodium gluconate

13.0 % in weight of triethanolamine

65.0 % in weight of deionized water

[4]The lubricant composition of Comparative Example 2 presents 0.25% in weight of the soap-based lubricant composition, such that the percent in weight of an average ethoxylation degree of 5 is 0.04%.

[3]AKYPO® RO 50 VG is an oleic ether carboxylate with an average ethoxylation degree of 5 commercialized by KAO Chemicals GmbH

Table 2 shows the friction coefficients obtained for the lubricant compositions described in Table 1. In this table, the lubricant compositions described in the present invention are included (LCC.1 - LCC.5), and also the Comparative Examples.

Table 2. – Friction coefficients (μ)

LCC	μ	[1]Foam
LCC.1	0.119	0
LCC.2	0.125	0
LCC.3	0.108	0
LCC.4	0.103	0
LCC.5	0.109	0
Comparative example 1	0.127	0
Comparative example 2	0.129	0

[1]Foam:

- Excess formation: 3
- Moderate formation: 2
- Slight formation: 1

- No formation: 0

From the experimental results it can be shown that the use of ether carboxylates according to the present invention not only permits lower friction coefficients to be obtained than those recorded for the comparative examples both in the acid and salt form, but also a zero foam formation.

Finally, it is noteworthy that the use of these ether carboxylates as lubricants in conveyor systems permits the use of bactericides to be reduced or eliminated as observed in trials for antiseptics and chemical disinfectants, which are shown below:

Example 2. Disinfectant effectiveness

Tests to measure the disinfectant effectiveness of different ethercarboxylates according to the invention against *Staphylococcus aureus ATCC 25923* was carried out following UNE-EN 1040 method (Chemical disinfectants and antiseptics. Basic bactericidal activity). All products were tested at 0.5 wt.-% active matter, at one-hour contact time. Samples tested and results are shown in the following table:

Table 3. – Disinfectant effectiveness

Lubricant	Result
Oleic ether carboxylate with an average ethoxylation degree of 1 as potassium salt	Pass*
Oleic ether carboxylate with an average ethoxylation degree of 1.5 as potassium salt	Pass*
Oleic ether carboxylate with an average ethoxylation degree of 2 as potassium salt	Pass*

**Pass: logarithm reduction > 10^5 cfu/mL*

CLAIMS

1. The use of ether carboxylates with an average ethoxylation degree of between 0.3 and 15 as a lubricant.

2. The use according to the previous Claim characterized because the ether carboxylates present general formula (I)

$R\text{-}(OCH_2CH_2)_n\text{-}O\text{-}CH_2COOX$ (I)

wherein

- R is an alkyl, alkenyl or alkynyl residue containing from 12 to 22 carbon atoms,
- n is a number between 0.3 and 15,
- X is hydrogen, an alkaline metal, an ammonium cation or an hydroxyalkylammonium cation.

3. Use according to Claim 2, characterized because in the general formula (I) R represents an alkyl, alkenyl or alkynyl residue containing from 16 to 18 carbon atoms.

4. Use according to Claims 2 and 3, characterized because in general formula (I) n is a number between 0.3 and 10.

5. Use according to Claims 2 to 4, characterized because in general formula (I) n is a number between 0.5 and 6.

6. Use according to Claims 2 to 5, characterized because in general formula (I) n is a number between 0.5 and 3.

7. Use according to any of Claims 2 to 6, characterized because in general formula (I) X is hydrogen or an alkaline metal.

8. Use according to any of the previous claims, characterized because the ether carboxylates are used as a lubricant agent in conveyor systems for glass and/or plastic bottles, such as, polyethylene terephtalate (PET) or polycarbonate bottles (PC).

9. Use according to Claims 1 to 7 characterized because the ether carboxylates are used as a lubricant agent in conveyor systems for cans, glass bottles, drums, cardboard containers and similar items.

INTERNATIONAL SEARCH REPORT

International Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C10M173/02
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C10M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 42 44 536 A (CLEANSO HYGIENE GMBH) 7 July 1994 (1994-07-07) cited in the application page 2, line 31 - page 3, line 10 claims; examples	1-9
X	EP 0 044 458 A (UNILEVER PLC ; UNILEVER NV (NL)) 27 January 1982 (1982-01-27) cited in the application page 3, line 1 - line 15 page 4, lines 1-3 claims; examples	1,8,9
X	DE 198 46 991 A (BACTRIA GMBH & CO KG INDUSTRIE) 20 April 2000 (2000-04-20) page 3, line 25 - line 38 claims; examples	1,8,9

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Dötterl, E

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INTERNATIONAL SEARCH REPORT

International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 747 431 A (GLOZBACH EBERHARD ET AL) 5 May 1998 (1998-05-05) cited in the application column 3, line 5 - line 55 claims; examples	1-9
X	US 4 895 668 A (DENTON JEFFREY ET AL) 23 January 1990 (1990-01-23) column 2, line 20 - column 3, line 15 claims; examples	1-9

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat[illegible] Application No
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